POSS Polymers for Space: Entrepreneurial Research

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14. ABSTRACT

The result of AFOSR-funded Enterpreneurial Research of Space Survivable Nanocomposites is presented. The focus is on AFRL/PRSM's effort in designing POSS-based nanocomposites. Corollary work on clay-based nanocomposites prepared by AFRL/MLBP were also produced under the same AFOSR effort at Wright-Patterson AFB.

15. SUBJECT TERMS
AFOSR; entrepreneurial research; space; nanocomposites; POSS; Polymer Working Group

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FOREWORD

This final technical report, entitled "POSS Polymers for Space: Entrepreneurial Research," presents the results of an in-house study performed under JON 23030026 by AFRL/PRSM, Edwards AFB CA. The Project Managers for the Air Force Research Laboratory were Dr. Shawn H. Phillips, Dr. Brent D. Viers, and Maj. Constance E. Schlaefer.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the SF Form 298.

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GLOSSARY

AFOSR: Air Force Office of Scientific Research
AFRL: Air Force Research Laboratory
AO: Atomic Oxygen
C: Carbon
CO_2:   carbon dioxide
CSD   Chemical Systems Division of Pratt and Whitney
DARPA   Defense Advanced Research Projects Agency
ER   Entrepreneurial Research Program
GEO   Geosynchronous Earth Orbit
H   Hydrogen
LEO   Low (altitude) Earth Orbit
MEO   Middle (altitude) Earth Orbit
ML   Materials Directorate, Air Force Research Laboratory
MISSE   Materials International Space Station Experiment
NASA   National Aeronautic and Space Administration
O   Oxygen
POSS   Polyhedral Oligomeric Silsesquioxane
PDMS   poly dimethyl siloxane or silicone
PR   Propulsion Directorate, Air Force Research Laboratory
PRSM   Propulsion Materials Branch, Air Force Research Laboratory
PWG   Polymer Working Group, AFRL/PRSM
$RSiO_{1.5}$ Silsesquioxane
R_2SiO_2 Silicone
SCEPTRE   Space Combined Effects Primary Test Facility, Materials Directorate AFRL.
Si   Silicon
SiO_2 Silica (glass)
UHV   Ultra High Vacuum
VUV   Vacuum Ultraviolet radiation
UV   Ultraviolet radiation
WPAFB   Wright Patterson Air Force Base
XPS   X-ray photoelectron spectroscopy

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1   RESEARCH OBJECTIVES

- To synthesize new nanocomposite polymers for potential high performance outer-space applications.
- To develop and test nanocomposite materials in extreme environments (vacuum ultraviolet radiation, Atomic Oxygen, outer space).
- To characterize the mechanisms for nanocomposite resistance to atomic oxygen.

2   HIGHLIGHTS OF AFRL/PRSM EFFORT

- Air Force Office of Scientific Research AFOSR Star Team Award for 6.1 Research.
- Air Force Research Laboratory-Propulsion Division (AFRL/PR) Program Manager of the Year: Dr. Shawn Phillips awarded for FY00.
- Polyhedral Oligomeric Silsesquioxane (POSS) modified -Kapton provides 9x improvement over space certified Kapton HN when exposed to high energy Atomic Oxygen (AO)-Professor Tim Minton, Montana State University and Professor Gar Hoflund, University of Florida
- POSS-Kapton, POSS-silicone, and POSS-urethanes exposed to outer space as part of NASA's Materials International Space Station Experiment. (MISSE)

3   AFRL/PR LABORATORY EFFORT

3.1   Introduction

The combination of the Air Force's strong commitment to space, NASA's continued programs for space exploration, and rapidly increasing commercial satellite production has resulted in a dire need for new light-weight, space-resistant materials with extended lifetimes. Unfortunately, aggressive environments encountered in every space mission have continually challenged the integrity of existing high-performance materials. Reported space environment damage to man-made bodies in orbit is staggering with numerous studies reporting that both radiation (atomic oxygen, vacuum ultraviolet, proton, electron and particle) damage and thermal cycling contribute to material degradation, which drastically reduces the lifetime of the orbiting body. In addition, significant reductions in the cost of launching payloads into space orbit ($6-10k/lb) cannot occur unless new materials are to perform multiple functions, an added dimension which has yet to be answered by the scientific community. Due to the extensive effort required, the development and testing of these new multi-functional materials is only possible with basic R&D funding and a concerted multi-lab effort within government laboratories.

Polymers are very attractive and desirable materials for use in space applications, particularly for addressing multi-functional requirements. With modifications these materials could potentially solve many of the weight-based and process-based problems plaguing the space industry and offer new capabilities for future systems. Polymers are remarkable materials but there are, as with any material, problems associated with their use, especially in a harsh space environment. Degradation is a prominent concern with using polymers in space. The high flux

of electromagnetic radiation and space-borne particles in earth orbit can wreak havoc on the stability of polymers. Bond scission and radical formation can lead to degradation and embrittlement. Also volatilization of some materials can lead to contamination of sensitive satellite components. An additional concern for many polymers is the inability to withstand the thermal cycling (–180 °C to 500 °C) experienced in orbit. Finally, polymers are typically not designed as structural materials. Although under normal operation in orbit loads are negligible, structures must withstand the high loads of launch and necessary orbital maneuvers.

Degradation of polymeric materials in the space environment is generally instigated from bombardment of electromagnetic radiation and atomic oxygen. Table 1 lists the bond dissociation energies for bonds found in commonly used space-qualified polymers Kapton® and FEP Teflon®. With the exception of the CF_2-F bond in FEP Teflon® the energies to break these bonds are very low, < 4.5 eV. Furthermore, the surfaces which face the direction of travel of spacecraft in low-earth orbit encounter atomic oxygen with collision energies of approximately 4.5 eV. An option to protect polymers from these environments is to deposit an inorganic coating. For commonly used inorganics (Table 1), bond dissociation energies tend to be much larger than those of organic polymers. The wavelength of electromagnetic radiation required to break these bonds represents less than 0.001% of the solar constant. However, failure of the coating either by mechanical or thermal cycling or micrometeor impacts will expose virgin material, resulting in rapid, localized degradation and subsequent system failure.

Table 1: Bond Dissociation Energies for Common Chemical Bonds Exposed to Outer Space

Bond	Dissociation Energy (eV)	λ (nm)	Material
-C_6H_4C(=O)-	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

Low-thermal expansion, space-resistant membranes and coatings are applications where nanocomposite polymers can have a significant impact for space-based systems. By combining the low weight and processibility of traditional polymers with the property enhancements observed from nanocomposite incorporation (high temperature stability, oxidation resistance, ceramic-layer formation) we propose to develop breakthrough elastomeric materials (e.g., polyurethanes, siloxanes) that will act as self-passivating/self-healing membranes that will dramatically increase the lifetime of orbiting bodies. Flammability studies, rocket motor insulation testing, and preliminary atomic oxygen results have shown that upon degradation, the hybrid organic/inorganic nanocomposites form a passivating Si-O layer. Failure of this passivation layer will expose more nanocomposites that will subsequently react with the environment to form a new protective layer, thereby self-healing the material. Furthermore, this Si-O layer is ceramic in nature and can rigidize the surface of the material, and potentially the entire polymer membrane. These nanocomposites will be synthesized by incorporating both

layered silicate and POSS nanotechnologies. The remarkable property enhancements as well as general flexibility to incorporate into any polymer matrix is why these two nanotechnologies are very promising candidates for space-resistant materials, and are detailed in the background and research plan sections of this proposal.

The goal of our research initiative is to develop these new nanocomposite materials for applications as multi-functional, space-resistant materials. These materials, as well as their successful integration hinge on the establishment of a fundamental understanding of the physical properties, environmental stability and processibility. The need for fundamental research, especially on novel polymeric materials, was identified by the Secretary of the Air Force-directed Scientific Advisory Board Report: New World Vistas as one of the most critical needs for the USAF R&D programs to enable continuation of technological superiority. The AFOSR's Entrepreneurial Research (ER) program for the Polymer Working Group (AFRL/PRSM) was to determine if POSS based nanocomposites are particularly suited to Air Force mission requirements by testing them in a variety of extreme environments (high vacuum, vacuum ultraviolet radiation (VUV/UHV), Atomic Oxygen (AO), reactive ion ablation, thermal cycling, etc.) One would naturally assume that POSS nanocomposites might serve as high performance Air Force/space materials. Previous flammability testing results have shown that POSS will pyrolize to a surface silica (Si-O) char layer. It was anticipated that POSS would also resist the rigors of space exposure, but there was no coherent program to provide the necessary characterization. The ER thrust was the formal program to address the synthesis and space-like environment testing of a variety of POSS-nanocomposites.

3.2   Methods, Assumptions, Proceedures.

3.2.1 Synthesis:

The incorporation of POSS into a variety of polymers is well documented [1-7] POSS-polyurethane and POSS-PDMS polymers were used as prepared from the published routes.[5-7] A specialty POSS-Kapton polymer (Figure 1) was synthesized as a variant on the theme of the traditional Kapton (pyromellitic dianhydride, PMDA-oxydianiline-ODA) synthesis. A cyclohexyl functionalized POSS-dianiline was specially provided to the PWG by Professor Frank Feher (University of California, Irvine), which was then solution polymerized via condensation techniques to produce a poly (amic acid), and then thermally imidized.[8] The polymer was identified by the loading of POSS (wt/wt) relative to the final polymer. It was not possible to measure the molecular weight of the POSS-Kapton, but the glass transition and glassy modulus of the control (POSS free) materials were consistent with literature values, and suggests that the material had polymerized to completion (degree of polymerization ca. 20) These polymers were solution cast into thin films for the simulated space testing. Further processing routes for the polymers were not formally addressed, but would be very important for industrial application of these materials.

3.2.2   Simulated Space Testing:

The unique University of Florida Atomic Oxygen Facility allows in-situ examination of sample changes under AO exposure. An electron stimulated desorption (ESD) source (Model OA10, Atom Sources, Inc.) compatible with ultrahigh vacuum (UHV), produces a high-purity, hyperthermal, O-atom flux greater than 10^{15} atoms cm^{-2} s^{-1} at a distance of 5 cm from the sample surface with an O atom: O$^+$ ratio of about 10^8. The ESD source is superior to plasma sources in that they produce hyperthermal, ground-state O atoms and operate at UHV pressures ($\sim10^{-9}$ torr) with negligible amounts of other species, including contaminants and UV radiation. Based on the measured ion energy distribution and mass spectrometric experiments, the neutral energy distribution is believed to have a maximum at about 5 eV with a full width at half maximum of about 3.6 eV [9,10]. In addition to combined cycle studies, the POSS and layered silicates will be characterized in-situ using XPS before and after incremental exposures to the flux produced by a novel electron stimulated desorption (ESD) atomic oxygen source [10]. Thin film samples of POSS-Kapton (0, 5, 10, 20% POSS) were spun cast onto germanium wafers and subjected to a very high energy (>5 eV) AO source in Professor Tim Minton's laboratory. The AO ablated polymers were characterized via profilometry (DekTak) to get a measure of the final erosion (relative to masked and unablated sections of the film).

To complement these LEO simulated environment studies, SCEPTRE provides simulated space exposure at mid and geosynchronous orbits using a UV solar simulator, a proton source and two electron sources which can be operated simultaneously. The SCEPTRE facility at WPAFB can also perform reflectance measurements *in-vacuo* to expedite data collection and eliminate the masking effects that air exposure can have when studying optical performance at orbital conditions. Degradation of different classes of materials proceeds by unique mechanisms with sensitivity toward a particular component or combination of components within the space environment.   Therefore, full exposure and parametric studies will be performed in the SCEPTRE facility to discern independent and synergistic effects of radiation exposure on polymeric materials. Surface chemical analysis of pre and post test specimens will be performed as outlined below. These data will be used to guide synthesis efforts for optimization of relevant mechanical and chemical properties for orbits of interest.

Of high importance in this program is the fundamental understanding of reaction mechanisms that occur when the polymer is exposed to a space environment. With this knowledge, polymers can be designed and optimized for applications at various orbital conditions and lifetimes to provide the necessary optical, physical, and mechanical properties. For example, LEO environments are dominated by AO while GEO environments are comprised of extreme solar UV with high energy electrons and protons present. With this in mind, optimal synthesis chemistry for a rigidizing polymer in LEO must incorporate mechanisms whereby AO induces the rigidization process while at GEO mechanisms highly reliant on UV must be designed into the polymer.

3.3 Results and Discussion*:*

Initial x-ray photoelectron (XPS) experiments on POSS-modified PDMS, or POSS modified polyurethane exposed to atomic oxygen were performed at the University of Florida AO facility. The changes in surface elemental composition and characteristic XPS peak positions confirmed that the silsesquioxane ($RSiO_{1.5}$) nanoparticle was able to incorporate the atomic oxygen to form a silica (SiO_2) protective layer. Visual comparison of the POSS-PDMS showed fewer surface microcracks than the PDMS control. Furthermore, the erosion could be characterized as "self healing," since if a segment of the silica protective layer was eroded (via ballistic impact, reactive ion undercutting, etc.) the high loading of the POSS and even dispersion (as evidenced by the high optical transparency) would provide new material to reform the protective layer. The limited amounts of the POSS-PDMS and POSS-urethanes precluded further investigation. Since the most prevalent polymers used in space applications are polyimides, and since atomic oxygen attack was identified as the main problem facing space polymers, the polymer working group of AFRL/PRSM decided to work exclusively on development of POSS based polyimide polymers.
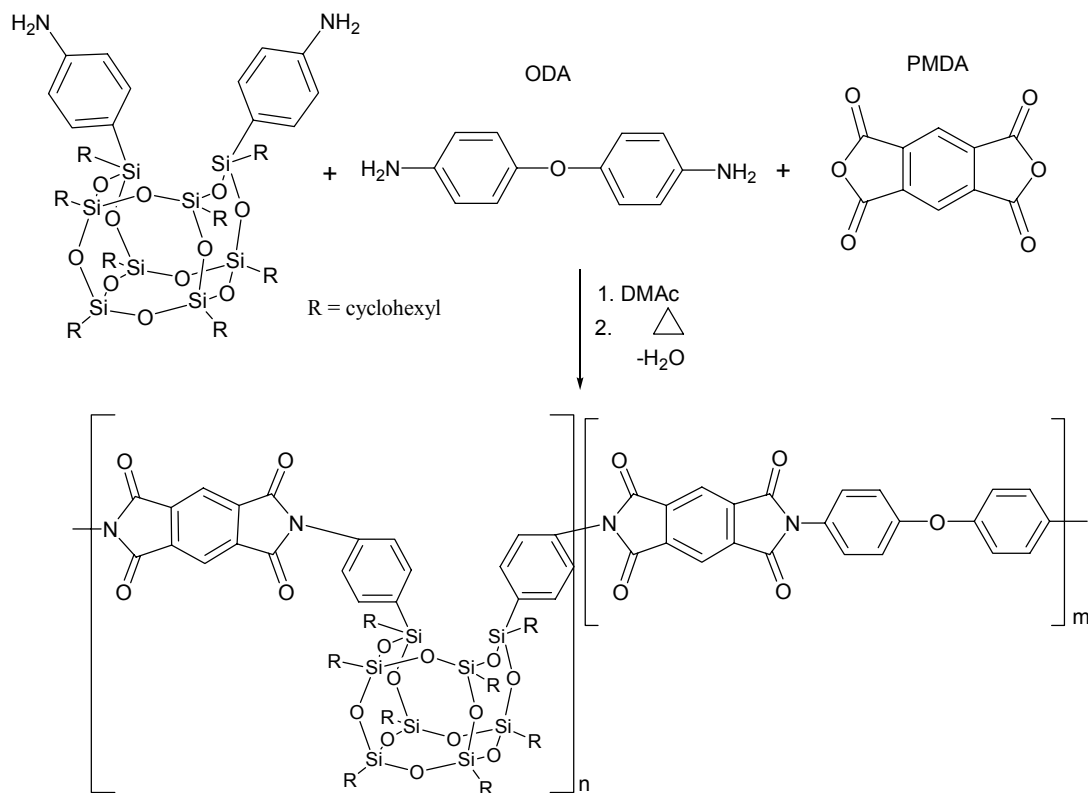

Figure 1: POSS-Polyimide Synthesis Scheme

Professor Hoflund (University of Florida) has built an atomic oxygen (AO) source for specialized testing. Atomic oxygen is generated by the electrically stimulated desoprtion of adsorbed oxygen atoms from a metallic surface. The flux of AO is 8×10^4 O atoms/cm^2·sec;

which is comparable to that in low earth orbit (LEO). This source (which is free from a strong UV background) will realistically simulate the LEO environment without serious artifacts; in addition, a variety of instrumentation has been coupled to the AO source to allow *in-situ* testing. It is particularly important that samples not be exposed to atmospheric oxygen for testing (as would occur when removing a sample from an AO chamber), since atmospheric oxygen is known to change the elemental composition of the surface layer. Such instrumentation (housed in a UHV environment) would include a number of surface specific analysis tools. The flux is currently being increased by a factor of 10-100x, so that a 4- to 40-day exposure would be equivalent to one year in LEO.

The ER funding has allowed for the study of AO resistance in polymers (and POSS polymers in particular). The carbonyl groups in Kapton apparently react with AO. These highly reactive bonds persist and react with humidity to enrich the near surface oxygen concentration. This effect can occur during routine handling of samples, which highlights the importance of studying materials *in-situ* as mentioned above. For a POSS-PDMS copolymer, the AO reacts with C and H in the near surface region forming a SiO_2 overlayer which protects the underlying polymer from further erosion. The same effect occurs in a POSS-polyurethane copolymer. The average energy of this ESD generated AO is 5eV (similar to that in LEO). This is greater than the common C-C and C-H bond energies, but less than what is seen in inorganic materials. This also emphasizes that sputtering ablation would be an important decomposition pathway. Professor Hoflund has planned a UV source upgrade to his AO chamber which will be used for characterization of POSS samples. Similarly, Professor Tim Minton (Montana State university) has further studied the physical ablation effects of very high energy (> 5eV) AO on POSS-based polyimides, as shown in Figure 1. Initial results have shown that the 10% POSS-Kapton materials have a 9x erosion resistance improvement relative to Kapton control. These incredible results have led to Professor Minton's generous offer to study other POSS polymers. Samples are planned for space certification-type experiments at the Aerospace Corporation. The testing of atomic oxygen, and particle bombardment (emulating GEO, MEO) will be undertaken by Aerospace Corp. Dr. Elisabeth Berman and Dr. Rich Vaia have planned a series of experiments at the SCEPTRE facility at WPAFB, where POSS materials will be exposed to VUV. Of course, the best model for space resistance will be for polymers actually exposed to outer space! Several POSS modified plastics (polyimides, and polyurethanes) were deployed on the international space station as part of the Materials International Space Station Experiment (MISSE) experiment. After years of space exposure, a post-mortem on a number of POSS-Polymers will show the degradation of the samples.

3.4   Conclusions

Polymers containing POSS nanostructures have proven to be extremely resistant to atomic oxygen. The mechanism for the enhanced resistance is that the silsesquioxane ($RSiO_{1.5}$) moiety apparently reacts with the oxygen to form a silica (SiO_2) protective layer. This mechanism was observed in a number of POSS-polymer nanocomposites: POSS-Kapton, POSS-PDMS and POSS-Polyurethane. Specialized X-ray photoelectron spectroscopy (XPS) testing shows the possible degradation pathways for polyimides under attack by atomic oxygen. However, POSS-Kapton has a 9x improvement in ablation resistance even under extremely high energy atomic oxygen attack (> 5 eV); thus, this material has great promise for a substitute for space resistant polymers. Finally, a number of collaborations and exotic sample testing (such as MISSE and

SCEPTRE) are underway, which should provide new insights as to material behavior under these rigorous conditions.

3.5 Recommendations

The ER program expired at the end of FY01. We were convinced that this ambitious project warranted a full research thrust; if not within AFRL, then with NASA or DARPA support. This work provided the foundation for a proposal to DARPA, which was accepted for FY04. Sponsored by Dr Leo Christodoulou, the new project seeks to develop more processable imide precursor monomers, fully characterize atomic oxygen erosion resistance, and ultimately space certify the modified material as a replacement for the current baseline Kapton. A key objective of the future research is to optimize the synthesis and processing to get high molecular weight films of POSS-polyimide of exceptional quality (having good ultimate properties, high POSS content, and optical properties.) Variants on the synthesis, incorporation of more flexible/processable imide precursor monomers, lower cost POSS monomers, etc. will be developed and tested. Beyond the current scope of the DARPA grant, novel uses of these systems for aerospace, high temperature, high performance adhesives to replace rivets, space structures etc., will be evaluated, via collaborative efforts with Aerospace Corporation and with academic collaborators.

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4 AFRL/PR PROGRAMMATIC SUMMARY

4.1 Program Funding

Table 1. Use of Funds ($K)

In-House	Capital Equipment	On-Site Contractor
30	70	100

Table 2. AFOSR Funding Profile ($K):

FY99	FY00	FY01
0	100	100

4.2 Personnel (total work effort on this project):

Air Force
  Shawn H. Phillips, Ph.D., Inorganic Polymer Science, 10%
  Brent D. Viers, Ph.D., Organic Polymer Science, 10%
  Capt Rene Gonzalez, M.S., Chemical Engineering, 100%
  Maj. Steven Svejda, Ph.D. Polymer Chemistry, 100%

On-Site Contractors

  Timothy S. Haddad, Ph.D., Inorganic Polymer Chemistry, 10%
  Patrick N. Ruth, H.S., Engineering 15%

Off-Site Contractors (total AFRL/AFOSR effort)

  Professor Frank J. Feher, Organometallic Chemistry, University of California Irvine, 15%
  Professor Patrick T. Mather, Ph.D., Materials Engineering, 20%
  Professor Gar Hoflund, Chemical Engineering, 10%, University of Florida
  Professor Ben S. Hsiao, Materials and Mechanics, 15%, SUNY
  Professor Richard M. Laine, Organometallic Chemistry, 20%, University of Michigan
  Dr. Jeffrey W. Gilman, Polymer Flammability, 10%, NIST
  Professor Tim Minton, Polymer Characterization, 10%, Montana State University

Laboratory Visitors:

> Dr. Steve Nutt, USC
> Dr. Tom Hahn, UCLA
> Dr. Tim Minton, Montana State University
> Dr's Joe Lichtenhan and Joe Schwab, Hybrid Plastics

5   REFERENCES (PUBLICATIONS, PRESENTATIONS, PROFESSIONAL ACTIVITIES)

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Haddad, T.S.; Mather, P.T.; Jeon H.G.; Phillips, S.H., "Hybrid Inorganic/Organic Diblock Copolymers. Nanostructure in Polyhedral Oligomeric Silsesquioxane Polynorbornenes", *Materials Research Society Symposium - Proceedings*, **628**, 2000, pp. CC2.6.1-CC2.6.7

5.3   Invention Disclosures and Patents

Blends of Polyhedral Oligosilsesquioxanes and Polyhedral Oligomeric Silicates with Ethylene-Based Copolymers and Flourinated Ethylene-Based Copolymers as Means to Control Elastomeric and Other Properties: Inventors: Hsiao, Phillips, Blanski, Fu. Filed 9/9/00

Nanostructured Chemicals as Alloying Agents in Polymers: Inventors: Lichtenhan, Schwab, Lee, Phillips. Filed 3/24/00

5.4   Presentations and Talks

Drs Shawn Phillips, Rusty Blanski, Tim Haddad and Andre Lee all presented talks at the Spring 2000 Materials Research Society Meeting in San Francisco, CA, April 2000.

Drs Rusty Blanski, Tim Haddad and Andre Lee presented talks at the Spring 2000 ACS Meeting in San Francisco, CA, March 2000.

Dr. Shawn Phillips presented two talks at the Spring 2000 Society for the Advancement of Material and Process Engineering, May 2000.

Dr. Shawn Phillips presented a talk at the Spring 2000 IHPRPT SC Meeting in Sacramento, CA, July 2000.

Dr. Shawn Phillips gave an invited lecture at SUNY in New York, November 1999.

Dr. Shawn Phillips gave a talk at over five different companies and over 20 different in-house lectures to visiting personnel.

5.5   Professional Activities

Journal Articles Reviewed for: Journal of Inorganic and Organometallic Polymers, Macromolecules, Journal of the American Chemical Society

Research Proposals Reviewed for: AFOSR sponsored University Research, PRDA for Solid Rocket Motors (Case, Insulation and Nozzles), STTRs, SBIR's

5.6   Honors (external and internal)

AFOSR Star Team Award (2-years)

Federal Laboratory Consortium Technology Transfer Award

R&D 100 Award (R&D Magazine)

Council for Chemical Research FY00 Government-Industry-University Collaboration Success Story

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APPENDIX A: FINAL REPORT FOR ER TASK
(AFRL/ML and AFRL/PR) Submitted to AFOSR

LRIR #: 00ML09ENT

Title: Development of Multi-Functional (Self-Passivating/Self-Healing) Polymeric Materials for Space-Survivable Structures and Membranes

Laboratory Task Manager: Dr. Richard Vaia (AFRL/MLBP) [Co-PIs: Dr. J. Sanders (AFRL/MLBT); Dr. S. Phillips (AFRL/PRSM); Dr. D. Marker (AFRL/DEBS)]
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E-mail Address: richard.vaia@wpafb.af.mil

AFOSR Program Manager: Dr. Charles Y-C. Lee

Research Objectives: The goal of this task is to synthesize and evaluate revolutionary new organic/inorganic materials that will form a self-passivating/self-healing coating upon exposure to Low Earth Orbit (LEO) or Geosynchronous Earth Orbit (GEO) environments.

Funding Profile ($K):

FY00	FY01
230	205

Program Summary:
The primary focus of this collaborative program between the Polymer Branch (Materials and Manufacturing Directorate), Propulsion Science and Advanced Concepts Division (Propulsion Directorate), Non-Structural Materials Branch (Materials and Manufacturing Directorate) and Optics and Imaging Division (Directed Energy Directorate) lies in developing materials containing inorganic nanoparticles that can survive simulated and actual space environment conditions. Efforts include i) synthesis and processing of inorganic/polymer nanomaterials based on dispersions of inorganic nanoparticles and/or incorporation of POSS-moieties; ii) characterization and evaluation of material durability to Low Earth Orbit (LEO) or Geosynchronous Earth Orbit (GEO) environments; and iii) evaluation of metrology and mechanical models to predict the mechanical response of complex hybrid films. Highlights from the three thrusts follows:

    Synthesis and Processing: An emulsion route to polymer nanocomposites was developed where addition of an aqueous dispersion of charged nanoparticles of opposite sense to the conventionally stabilized emulsion results in an ion exchange reaction at the latex surface and subsequent absorption of nanoparticle. Substantial increase in rubbery modulus (~200%) and heat distortion temperature (20°C) for only 1% PS-PBI in PMMA was observed. In addition, new synthetic methodologies were developed for the synthesis of two POSS elastomers and POSS-kapton. For the POSS-PDMS, a difunctional POSS

monomer was co-condensed with the PDMS monomers to form a bead polymer. POSS-polyurethanes were co-condensed to form pendant polymers containing 20 and 60 wt. % POSS.

Durability: To examine material behavior in low earth orbit, an atomic oxygen generator within a space simulation chamber equipped with in-situ characterization instrumentation was built. The AO resistance of POSS co-polymers, including Kapton, urethane and PDMS, was examined. Atomic Oxygen studies, followed by in-situ XPS analysis clearly show the formation of a protective SiO_2 layer that prevents further AO degradation. Varying the wt.% POSS (20 and 60%) in the POSS-polyurethanes demonstrated that only the time for SiO_2 formation is affected by nanocomposite incorporation. In conjunction, investigation of nanocomposite durability to ozone and plasma demonstrated the formation of a self-passivating inorganic coating that drastically reduces the erosion rate by more than an order of magnitude. The formation of a self-passivating inorganic coating was shown to be a general property, occurring in many systems including epoxy, nylon and polyolefins nanocomposites. To examine material behavior in GEO, modification of existing space simulation chambers enable qualitative evaluation of material performance in UV and electron environments. Material studies are currently underway with this new characterization system.

Metrology: Optical performance of membranes comprised of commercially available films was evaluated to base-line performance of future hybrid systems.

The ER program was completed in FY01. The initial groundwork laid during this ER has provided the infrastructure and expertise to evaluate polymer-based material systems in various space environments, and thus provide a needed capability for new materials development. Research in FY02 will finalize the characterization of the materials discussed above in various exposure environments. Additionally, initial experiments by Professor Tim Minton (Univ. Montana) has indicated that POSS based polyimides exhibit a 9x improvement in erosion resistance relative to a Kapton control for very high energy (> 5eV) AO. These studies will continue. Samples are also in the queue at Aerospace Corporation to certify materials for space applications in MEO and GEO. Finally, the POSS and nanocomposite materials deployed on the international space station as part of the Materials International Space Station Experiment (MISSE) experiment will be returned in 2002, characterized and compared to the ground-based results provided by this program.

During the program, 11 journal articles (7 refereed), 9 presentations (2 invited) and 2 patent disclosures with task personnel were recorded.

Publications (Refereed):

R.A. Vaia and E.P. Giannelis, "Polymer nanocomposites - Status and opportunities," MRS Bulletin, 26, 394 (2001)

Phillips, S.H., Hoflund, G.B., Gonzalez, R.I. "Remarkable AO Resistance of POSS Inorganic/Organic Polymer" 45th International SAMPE Symposium, 45, 1921 (2000).

Gilman, J.W., Hilton, D., Phillips, S.H., et. al. "Flammability Properties of Polymer-Layered-Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites" Chemistry of Materials, 12, 1866, (2000).

Gonzalez, R.I., Phillips, S.H., Hoflund, G.B., "In-Situ Oxygen-Atom Erosion Study of a Polyhedral Oligomeric Silsesquioxane-Siloxane Copolymer" Journal of Spacecraft and Rockets, 37, 463, (2000).

Jeon, H.G.,; Mather, P.T.; Haddad, T.S. "Shape Memory and Nanostructure in Poly(norbornyl-POSS) Copolymers" Polymer International, 49, 453 (2000).

Publications (Submitted):

H. Fong, R.A. Vaia, J.H. Sanders, D.M. Lincoln, P.J. John, A.J. Vreugdenhil, J. Bultman, C.A. Cerbus, and H.G. Jeon, "Formation of self-generating, inorganic passivation layer on nylon 6 / layered silicate nanocomposite," Chem. Mater., (2001) in press.

Hoflund, G. B., Gonzalez, R. I., Phillips, S. H., "In-situ Oxygen Atom Erosion Study of a Polyhedral Oligomeric Silsesquioxane-Polyurethane Copolymer," Journal of Adhesion Science and Technology, (2001) in press.

Publications (Unrefereed):

H. Fong, R.A. Vaia, J.H. Sanders, D.M. Lincoln, P.J. John, A.J. Vreugdenhil, J. Bultman, C.A. Cerbus, and H.G. Jeon, "Formation of self-generating, inorganic passivation layer on nylon 6 / layered silicate nanocomposite," Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 42, 354 (2001)

G. B. Rossi, G. Beaucage, T.D. Dang and R. Vaia, "Emulsion Technique for Polymer-based Molecular and Nanocomposites," Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 42(2), 29 (2001)

Blanski, R. L.; Phillips, S. H.; Chaffee, K.; Lichtenhan, J. D.; Lee, A.: Geng, H. P., "The Preparation and Properties of Organic/Inorganic Hybrid Materials by Blending Polyhedral Oligosilsesquioxanes into Organic Polymers" Polymer Preprints, 41, 585, (2000).

Fu, B. X.; Zang, W.; Hsiao, B. S.; Johansson, G.; Sauer, B.B.; Phillips, S. H.; Blanski, R. L.; Rafailovich, M.; Sokolov, J., "Synthesis and Characterization of Novel Segmented Polyurethanes Containing Polyhedral Oligomeric Silsesquioxanes (POSS) Nanostructural Molecules" Polymer Preprints, 41, 587, (2000).

Invention Disclosures and Patents

Blends of Polyhedral Oligosilsesquioxanes and Polyhedral Oligomeric Silicates with Ethylene-Based Copolymers and Flourinated Ethylene-Based Copolymers as Means to Control Elastomeric and Other Properties: Inventors: Hsiao, Phillips, Blanski, Fu. Filed 9/9/00

Nanostructured Chemicals as Alloying Agents in Polymers: Inventors: Lichtenhan, Schwab, Lee, Phillips. Filed 3/24/00

Lectures, Presentations, Talks (*indicates invited presentation):

H. Fong, R.A. Vaia, J.H. Sanders, D.M. Lincoln, P.J. John, A.J. Vreugdenhil, J. Bultman, C.A. Cerbus, and H.G. Jeon, "Formation of Self-Generating, Inorganic Passivation Layer on Nylon 6 / Layered Silicate Nanocomposite," 221th National Meeting, American Chemical Society, San Diego, CA (March 2001).

G. B. Rossi, G. Beaucage, T.D. Dang and R. Vaia, "Emulsion Technique for Polymer-based Molecular and Nanocomposites," 222th National Meeting, American Chemical Society, Chicago, IL (August 2001).

G. B. Rossi, G. Beaucage, T.D. Dang and R. Vaia, "Fabrication of Rod-Coil Nanocomposites via Emulsion Technique," March Meeting, American Physics Society, Seattle WA (March 2001).

W.W. Adams, T.J. Bunning, B.L. Farmer, R.A. Vaia, K.M. Kearns, T. Banerjee, and H.G. Jeon, "Investigations of Novel Methods to Extend the Use Temperature of Polymers," ACS Pacificchem 2001, Honolulu, HI (December 2000)

* R.A. Vaia, "Polymer Nanocomposites for Extreme Environments," National Space and Missiles Materials Symposium, Monterrey, CA (June 2001).

Rene I. Gonzalez, Steven A. Svejda, Shawn H. Phillips, and Gar B. Hoflund, "Surface Studies of Space-Survivable Hybrid Organic/Inorganic Polymers," 222nd ACS National Meeting Chicago, (August 2001).

* Rene I. Gonzalez, Steven A. Svejda, Shawn H. Phillips, and Gar B. Hoflund "Synthesis and Surface Studies of Space-Survivable Polyhedral Oligomeric Silsesquioxane Copolymers," University of Chicago, Chemistry Department, (August 2001).

Shawn H. Phillips, Rene I. Gonzalez, Kevin P. Chaffee, Timothy S. Haddad. "Remarkable AO Resistance of POSS Inorganic/Organic Polymers," 45th International SAMPE Symposium, (May 2001).

Gar B. Hoflund, Rene I. Gonzalez, Shawn H. Phillips. "Space Durable and Atomic Oxygen Resistant POSS Polymers," Nanostructured Chemicals Workshop, Huntington Beach CA (October 2000).

APPENDIX B: SUPPORTING TECHNICAL PAPERS

Gonzalez, R.I., Phillips, S.H., Hoflund, G.B., "In-Situ Oxygen-Atom Erosion Study of a Polyhedral Oligomeric Silsesquioxane-Siloxane Copolymer," *Journal of Spacecraft and Rockets,* **37 (4)**, 2000, pp. 463-467.

Hoflund, G.B., Gonzalez, R.I., and Phillips, S.H., "In situ oxygen atom erosion study of a polyhedral oligomeric silsesquioxane-polyurethane copolymer," *J. Adhesion Sci. Technol.,* **15(10),** 2001, pp. 1199-1211.

In Situ Oxygen–Atom Erosion Study of Polyhedral Oligomeric Silsesquioxane-Siloxane Copolymer

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and
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University of Florida, Gainesville, Florida 32611

The surface of a polyhedral oligomeric silsesquioxane-siloxane copolymer film has been characterized in situ by using x-ray photoelectron spectroscopy before and after exposure to incremental fluences of oxygen atoms produced by a hyperthermal oxygen atom source. The data indicate that the atomic oxygen initially attacks the cyclohexyl groups that surround the polyhedral oligomeric silsesquioxane cage, resulting in the formation and desorption of CO_2 from the surface. The carbon concentration in the near-surface region is reduced from 65.0 at% for the as-entered surface to 16.3 at% following 63 h of O-atom exposure at a flux of 2×10^{13} O atoms/cm² s. The oxygen and silicon concentrations are increased with incremental exposures to the O-atom flux, but the rates of increase slow with increased exposure. The oxygen concentration increases from 18.5 at% for the as-entered sample to 55.7 at% following the 63-h exposure, and the silicon concentration increases from 16.6 to 28.0 at%. The data reveal the formation of a silica layer on the surface, which serves as a protective barrier preventing further degradation of the underlying polymer with increased exposure to the O-atom flux.

Introduction

THE aggressive conditions present in low Earth orbit (LEO) at altitudes ranging from 200 to 700 km in the ionosphere reduce the longevity of organic materials used in the construction of space vehicles, thereby restricting the number of space-certified materials. The predominant environmental species in LEO responsible for this material degradation is atomic oxygen (AO).[1–4] AO is formed by the dissociation of molecular oxygen by ultraviolet radiation from the sun, resulting in an AO concentration of approximately 10^8 atoms/cm³. The reverse reaction in which an oxygen molecule forms from AO does not have a high reaction rate because it requires a teratomic collision. The third atom is required to carry away the energy released by the formation of O_2. For this reason the predominant species in LEO is AO. The actual flux of the impingement of $\sim 10^{15}$ atoms/cm² s on a spacecraft is high as a result of orbiting speeds of approximately 8 km/s. At these relative speeds AO particles collide with a kinetic energy of ~ 5 eV (Refs. 5–7). The effect of AO on spacecraft material degradation has been studied on space-exposed materials (in STS missions and at the NASA Long Duration Exposure Facility, or LDEF)[1,8,9] and in simulation facilities.[10–12] In these studies the samples were analyzed by x-ray photoelectron spectroscopy (XPS) but only after the AO-treated samples were exposed to air. Recent studies have shown that exposure to air chemically alters the reactive surfaces formed during AO exposure.[13,14] Therefore, in situ AO erosion studies of polymers must be performed to avoid artifacts induced by air exposure.

In this study a thin film of polyhedral oligomeric silsesquioxane (POSS)-siloxane copolymer has been characterized in situ by using XPS before and after incremental exposures to the flux produced by an electron-stimulated desorption (ESD) atomic oxygen source.[15] POSS molecules are hybrid inorganic–organic structures synthesized from the self-condensation reactions of alkyl trichlorosilanes. Over the past seven years, Lichtenhan and coworkers[16–20] have focused on incorporating POSS frameworks into traditional polymer systems by means of copolymerization, grafting, and blending processes. Significant property enhancements have been reported for these hybrid polymers, including an increased use temperature, increased toughness, decreased flammability, and increased oxidation resistance. These property enhancements are attributed to the nanolevel interaction of the POSS framework with the polymer matrix. Traditionally, silica fillers have been used in polymer applications requiring alterations in physical and mechanical properties such as tensile strength, abrasion, and fatigue resistance. In addition to numerous property enhancements, POSS polymers have lower densities (1.2–1.5 g/ml) than silica fillers (2.4–2.6 g/ml) (Refs. 21 and 22). Unlike silica fillers, POSS frameworks can be easily functionalized for polymer compatibility without significantly affecting processing conditions. Compared with silica fillers, POSS hybrid polymers are able to impart similar property enhancements, including many not possible with the use of filler technology. Previous studies have also shown that Si-O systems exhibit a superior resistance to AO degradation, partly because of their oxophilicity and high bond strength (~ 8 eV) (Refs. 23 and 24). However, pure siloxane systems have displayed many disadvantages for space applications, including the generation of a volatile cyclic species when exposed to AO that can recondense on optical surfaces.[25] The present study details the results obtained from exposing a POSS-polydimethylsiloxane (PDMS) film to a simulated LEO environment. Specifically, it describes the formation of a protective silica layer with exposure to an O-atom flux. This layer serves as a protective barrier, preventing further degradation of the underlying polymer with increased AO exposure.

Experimental

O-Atom Source Characteristics

The ESD source used in this study was developed by Hoflund and Weaver[15] and is commercially available through Atom Sources, Inc. It is ultrahigh vacuum (UHV) compatible, operates with the sample at room temperature, and produces a high-purity, hyperthermal, AO flux with an O atom:O^+ ratio of $\sim 10^8$. These sources are superior to plasma sources in that they produce hyperthermal, ground-state O atoms and operate at UHV pressures ($\sim 10^{-9}$ torr) with negligible amounts of other species, including ions, contaminants, and UV radiation. The operational concept of the hyperthermal oxygen atom generator is shown in Fig. 1. Ultrahigh-purity molecular O_2 dissociatively adsorbs on a metallic Ag alloy membrane at the high-pressure side and permeates at elevated temperature (~ 400°C) to the UHV side. There the adsorbed atoms are struck by a directed flux of primary electrons, which results in ESD of O atoms forming
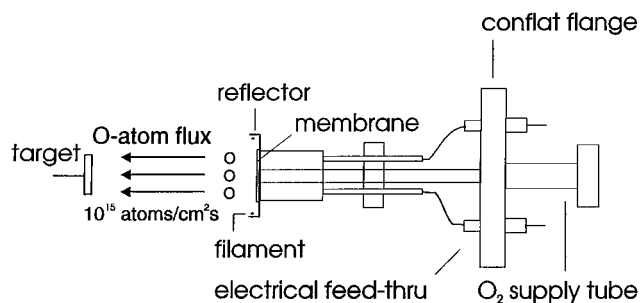
Fig. 1 Schematic diagram of the atom source.

Fig. 2 Scheme for synthesis of the POSS-PDMS copolymer used in this study.

a continuous flux. Many processes have to function in series at sufficiently high rates for the system to work, including dissociative adsorption of the molecular gas on the metal surface, permeation of atoms through the membrane, and formation of the neutral flux by ESD. Some bremsstrahlung radiation is produced by the electrons' striking the Ag membrane. Because the UV component is small, this radiation has only a small effect on the chemical processes occurring at the sample surface. Another potential problem is the sublimation of Ag from the membrane surface, which could accumulate on the sample surface. Studies have been performed to optimize the power input to the membrane surface so that the O flux is maximized while the Ag sublimation rate is negligible. This is possible because the Ag sublimation rate decreases exponentially with temperature.

The O atoms produced by this source have been shown to be hyperthermal, but their energy distribution has not been measured. Corallo et al.[26] measured the energy distribution of O ions emitted by ESD from a Ag (110) surface and found that this distribution has a maximum of ~5 eV and a full width at half-maximum of 3.6 eV. This ion energy distribution would set an upper bound for the neutral energy distribution because ESD neutrals are generally believed to be less energetic than ESD ions. This point has been discussed often in the ESD literature but not actually demonstrated. A mass spectrometer has been used to characterize the flux produced by this ESD source. The ion acceleration potential was set at 0.0 V in these studies. Because calibration studies demonstrated that the ions entering the quadrupole section had to have a minimum kinetic energy of 2.0 eV to reach the detector, the ESD neutrals have a minimum energy of 2 eV. Therefore, the hyperthermal AO produced by this ESD source has an energy higher than 2 eV but lower than the ion energy distribution.

Preparation of the POSS-PDMS Copolymer

The POSS siloxane copolymer used in this study and shown in Fig. 2a was synthesized by using a method similar to that described by Lichtenhan et al.[27] and Gilman et al.[28] The diol-silsesquioxane monomer (5.00 g or 4.54 mmol) shown in Fig. 2b was dissolved in 10 ml of tetrahydrofuran (THF) in a 50-ml flask to which 1.98 g (4.54 mmol) of bis(dimethylamino)polydimethylsiloxane (approximately 4.9 silanes per oligomer, $Mw = 435.5$ g/mol) was added with an additional 15 ml of THF. The reaction mixture was stirred and heated to 65°C under nitrogen for 48 h. The polymer was then precipitated into 350 ml of methanol, stirred for 2 h, and filtered and air dried for 12 h. To end cap the polymer with trimethylsilane, it was dissolved in 25 ml of THF with an excess of N,N-(dimethylamino)trimethylsilane and reacted at 65°C under nitrogen for another 48 h. The polymer was again precipitated into 350 ml of methanol. After decanting the solvent, fresh methanol with dilute HCl was added to neutralize any excess amine. The solution was again decanted, and the remaining white solid was dried under vacuum for 2 h, producing a yield of 6.27 g (95% theoretical yield). Molecular weights were determined from multiangle laser light-scattering measurements obtained from a DAWN-F detector (Wyatt Technologies) equipped with a gel-permeation chromatography column. The number average molecular weight, mass average molecular weight, and degree of polymerization were found to be 62,000, 118,000, and 43, respectively. A peak area analysis of the ^{29}Si nuclear magnetic resonance (NMR) 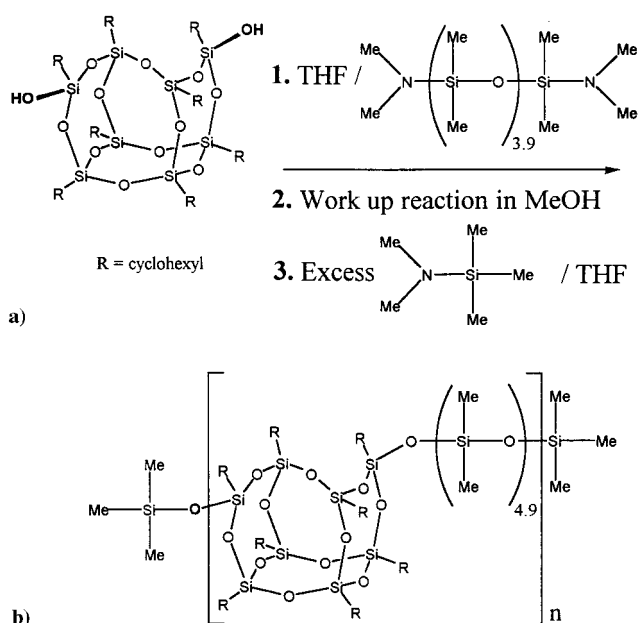data gives a degree of polymerization of 38 and shows on average 4.8 SiMe$_2$ groups per repeat unit. Relevant peaks in the ^{29}Si NMR spectrum are a singlet at 7.2 parts in 10^3 (ppm) (Me$_3$Si endgroups, peak area of 2.0); a multiplet at 21.5 ppm (Me$_2$Si-O, peak area of 184); and four singlets at 66.39, 68.13, 68.20, and 69.51 ppm (POSS, peak area of 305.6).

Preparation of Thin Films by Solvent Casting

Thin films of the trimethylsilane-terminated POSS-PDMS were made by dissolving 100 mg of the coarse powder in 15–20 ml of THF, solvent casting onto 1 × 1 cm aluminum substrates, and drying at room temperature for 24 h. The aluminum substrates were prepared and cleaned with Boraxo soap and water, and then deionized water followed by ultrasonic cleaning in toluene, acetone, trichloroethylene, acetone, and ethanol, respectively.

Surface Characterization

A solvent-casted POSS-PDMS film was wiped with isopropanol and inserted into the UHV chamber (base pressure $< 10^{-10}$ torr). XPS was performed by using a double-pass cylindrical mirror analyzer (DPCMA; PHI Model 25-270AR). XPS survey spectra were taken in the retarding mode with a pass energy of 50 eV, and high-resolution XPS spectra were taken with a pass energy of 25 eV by using Mg Kα x-rays (PHI Model 04-151 x ray source). Data collection was accomplished by using a computer interfaced, digital pulse-counting circuit[29] followed by smoothing with digital-filtering techniques.[30] The sample was tilted 30 deg off the axis of the DPCMA, and the DPCMA accepted electrons emitted into a cone 42.6 ± 6 deg off the DPCMA axis.

XPS spectra were first obtained from the as-entered, solvent-cleaned sample. The sample was then transferred by means of a magnetically coupled rotary–linear manipulator into an adjoining UHV chamber that houses the ESD AO source. There the surface was exposed to the hyperthermal AO flux and reexamined without air exposure after total exposure times of 2, 24.6, and 63 h. The approximate normal distance between the sample face and source in this study was 15 cm, at which distance the flux was approximately 2×10^{13} atoms/cm^2 s for the instrument settings used. The substrate temperature was determined with a chrome-alumel thermocouple attached to the Al substrate. At this distance the sample remained at room temperature during the AO exposures. The sample temperature did increase to 50°C during XPS data collection. After the 63-h AO exposure, the sample was exposed to air (room temperature ~22°C and relative humidity ~60%) for 4.75 h and again examined by using XPS.

Results and Discussion

XPS survey spectra obtained from a solvent-wiped POSS-PDMS surface before and after the 2-, 24.6-, and 63-h AO exposures are shown in Figs. 3a–3d, respectively. Spectrum e in Fig. 3 was taken after the 4.75-h air exposure following the 63-h AO treatment. The peak assignments shown in Fig. 4 pertain to all five spectra. The predominant peaks apparent in these spectra include the C $1s$, O $1s$, Si $2p$, Si $2s$, O $2s$, and O Auger peaks. No Ag features are apparent in these spectra. Significant changes in relative peak heights are observed for the C, O, and Si features following the O-atom exposures. An estimate of the near-surface compositions has been calculated from the peak areas in the survey spectra by assuming that this region is homogeneous and by using published atomic sensitivity factors.[31] The compositions determined in this manner are presented in Table 1 for the as-entered, AO-exposed, and air-exposed surfaces. XPS probes the near-surface region of the sample and yields a weighted average composition, with the atomic layers near the surface being weighted more heavily because these photoemitted electrons have a lower probability of scattering inelastically. The sampling depth is ~30 atomic layers, and ~10% of the signal originates from the outermost atomic layer.[32] This near-surface region is nonhomogeneous because the AO reacts with the outermost few atomic layers. Therefore, the region that is affected to the greatest extent as a result of the reaction with AO also makes the largest contribution to the XPS signal. This fact implies that XPS is an

Table 1   Near-surface composition determined from XPS data obtained from the as-entered, solvent-cleaned, and AO and air-exposed POSS-PDMS sample

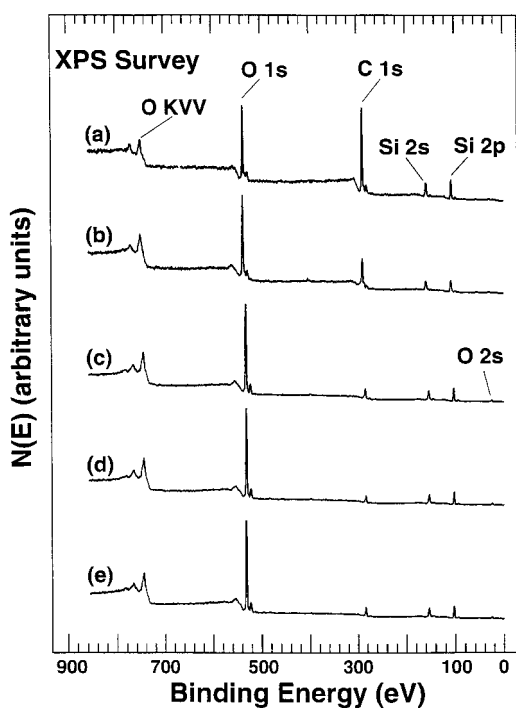| Surface sample treatment	AO fluence, O/cm²	Composition, at%			Atom ratio O/Si
		O	C	Si	
As entered, solvent cleaned	——	18.5	65.0	16.6	1.11
2-h AO exposure	1.44×10^{17}	33.8	48.4	17.8	1.90
24.6-h AO exposure	1.77×10^{18}	49.1	22.1	28.8	1.70
63-h AO exposure	4.53×10^{18}	55.7	16.3	28.0	1.99
4.75-h air exposure following the 63-h AO exposure	4.53×10^{18}	52.8	19.5	27.7	1.91

Fig. 3   XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film after a) insertion into the vacuum system; b) 2-h, c) 24.6-h, and d) 63-h exposures to the hyperthermal AO flux; and e) 4.75-h air exposure following the 63-h AO exposure.

Fig. 4   XPS C $1s$ spectra obtained from a solvent-cleaned, POSS-PDMS film after a) insertion into the vacuum system; b) 2-h, c) 24.6-h, and 63-h exposures to the hyperthermal AO flux; and e) 4.75-h air exposure following the 63-h AO exposure.
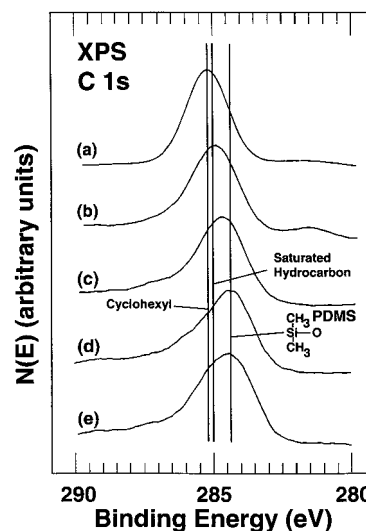
excellent technique for studying the AO erosion of spacecraft materials. Even though the distribution functions involving the depth of chemical reactions in the near-surface region and the XPS determination of the weighted average composition of the near-surface region are complex, the compositional values, determined by using the homogeneous assumption and shown in Table 1 as a function of AO fluence, provide a trend that is indicative of the chemical alterations occurring during AO exposure. This trend is supported by the chemical state alterations determined by XPS, which are discussed next. The O-to-Si atomic ratio is 1.11 for the as-entered sample; it is increased to 1.90 after the 2-h exposure, then reduced to 1.70 after 24.6 h, and increased again to 1.99 after the 63-h O-atom exposures. This behavior indicates that complex chemical reactions occur during AO exposure. After the 4.75-h air exposure the O-to-Si atomic ratio is 1.91. These changes in the O-to-Si atomic ratio resulting from exposure to the AO flux indicate the formation of SiO_2 and are consistent with the high-resolution spectra that follow. A large reduction in the C $1s$ peak is observed as a result of the incremental exposures to the AO flux. The near-surface C concentration decreases from 65.0 at% for the as-entered sample to 16.3 at% after the 63-h exposure. This decrease is caused by the reaction of C in the near-surface region with O to form CO_2. A small increase in the carbon content to 19.5 at% is observed after exposure to air for 4.75 h, probably as a result of the adsorption of C-containing molecules such as hydrocarbons from the air. Hydrogen in the POSS-PDMS would also react with the AO to form water, which would desorb.

High-resolution XPS C $1s$, O $1s$, and Si $2p$ obtained from the as-received, solvent-wiped surface before and after the 2-, 24.6-, and 63-h AO exposures are shown in spectra a–d of Figs. 4, 5, and 6, respectively. Spectrum e was obtained after the 4.75-h air exposure following the 63-h O-atom exposure. Variations in peak shapes and positions are observed between the nonexposed, AO-exposed, and air-exposed surfaces, indicating that the chemical species distribution is altered by exposure to the AO flux and then to air.

The C $1s$ peak shown in Fig. 4a is centered at 285.2 eV, indicating that the predominant form of carbon present for the as-entered sample is in the form of a fully substituted hydrocarbon, that is, the cyclohexyl groups on the POSS cage.[33] In spectra b, c, and d the C $1s$ peak becomes broader, and the peak center shifts to a lower binding energy (BE) with increasing exposure to the AO flux. After the 63-h exposure, the C $1s$ has a BE of 284.4 eV. This value is characteristic of methyl groups on the PDMS chain.[33] The fact that these changes coincide with a decrease in the total carbon concentration in the near-surface region from 64.1 to 13.5 at% implies that the cyclohexyl groups are being removed selectively, leaving the methyl groups. This selective removal is caused by the larger size of the POSS cage (1.5 nm) compared with the PDMS chain as
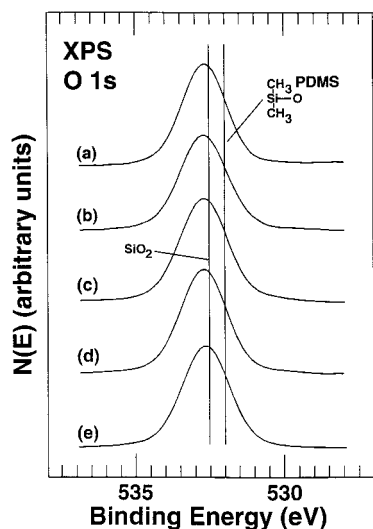
Fig. 5 XPS O 1s spectra obtained from a solvent-cleaned, POSS-PDMS film after a) insertion into the vacuum system; b) 2-h, c) 24.6-h, and d) 63-h exposures to the hyperthermal AO flux; and e) 4.75-h air exposure following the 63-h AO exposure.
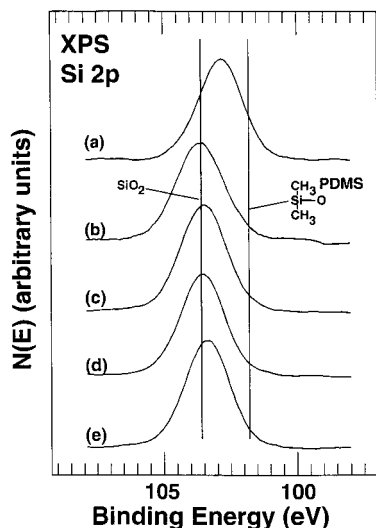

Fig. 6 XPS Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film after a) insertion into the vacuum system; b) 2-h, c) 24.6-h, and d) 63-h exposures to the hyperthermal AO flux; and e) 4.75-h air exposure following the 63-h AO exposure.

shown in Fig. 2. Small shoulders are visible on the high-BE side of the C 1s peak in spectra b, c, and d. These probably are from species such as alcohols, formaldehydes (BE ~286.0–287.7 eV), and organic acids (BE ~287.5) that form by reaction with the AO flux. Exposure to air (spectrum e) produces an increase in the shoulder near 285.0 eV, indicating adsorption of hydrocarbons from the air at reactive surface sites produced during the AO exposure. This observation is consistent with the increase in the C concentration after the air exposure, as shown in Table 1.

The O 1s spectra obtained from the sample before and after the various treatments are shown in Fig. 5. These peaks are broad, indicating that various chemical states of oxygen are present. After the 2-h exposure to the AO flux, the contribution from oxygen is significantly increased from 18.5 to 33.8 at%, and then it increases further to 49.1 and 55.7 at% after the 24.6- and 63-h exposures, respectively. However, the peak shapes and positions do not change much with treatment indicating that the O-containing species have closely spaced O 1s BEs. A previous XPS study of PDMS has shown that the oxygen in the PDMS chain has a BE of 532.0 eV (Ref. 33), whereas SiO_2 has a BE of ~532.5 eV (Ref. 33).

The Si 2p peaks obtained from the sample before and after the various treatments are shown in Fig. 6. Similar to the O 1s peak, the Si 2p peak for the as-entered sample (spectrum a) is broad, indicating the presence of several chemical states of silicon. This peak is centered at a BE of 102.7 eV, which corresponds to $RSiO_{1.5}$ in the POSS cage. However, spectra b, c, and d reveal the formation of a SiO_2 layer with incremental exposures to the AO flux. The fact that little difference is observed in the spectra obtained after the 24.6- and 63-h exposures indicates that this silica layer forms a protective barrier on the surface that prevents further degradation of the polymer with longer exposure to the AO flux. The significant compositional changes observed indicate that most of the near-surface region examined by XPS is altered by the AO exposure. The chemical reactions that form CO_2 and H_2O are exothermic so that the local surface temperature may be relatively high. This fact and the fact that the AO provides a chemically induced driving force at the surface result in diffusion of subsurface C and H to the surface where they react with the AO. This mechanism is responsible for the subsurface compositional alterations observed by using XPS and for the formation of a relatively thick SiO_2 layer.

Conclusion

The surface of a POSS-PDMS copolymer film has been characterized in situ by using XPS before and after exposure to different fluences of AO produced by an ESD hyperthermal oxygen atom source. The XPS data indicate that the carbon content of the near-surface region is decreased from 65.0 to 16.3 at% after a 63-h exposure to an AO flux of 2×10^{13} atoms/cm^2 s. The oxygen and silicon concentrations in the near-surface region increase with increasing exposure to the AO flux, with the oxygen-to-silicon atom ratio increasing from 1.11 for the as-entered sample to 1.99 after a 63-h AO exposure. High-resolution XPS data suggest that the AO initially attacks the cyclohexyl groups on the POSS cage forming CO_2 and H_2O, which desorb. Increased exposure to the AO flux results in the formation of a silica layer on the surface, which acts a protective barrier preventing further degradation of the underlying polymer.

Acknowledgments

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In situ oxygen atom erosion study of a polyhedral oligomeric silsesquioxane–polyurethane copolymer [*]

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Abstract—The surface of a polyhedral oligomeric silsesquioxane–polyurethane copolymer has been characterized *in situ* using X-ray photoelectron spectroscopy before and after exposure to incremental fluences of oxygen atoms produced by a hyperthermal oxygen atom source. The data indicate that the atomic oxygen initially attacks the cyclopentyl groups that surround the polyhedral oligomeric silsesquioxane cage most likely resulting in the formation and desorption of CO and/or CO_2 and H_2O from the surface. The carbon concentration in the near-surface region is reduced from 72.5 at.% for the as-entered surface to 37.8 at.% following 63 h of O-atom exposure at a flux of 2.0×10^{13} O atom/cm^2-s. The oxygen and silicon concentrations are increased with incremental exposures to the O-atom flux. The oxygen concentration increases from 18.5 at.% for the as-entered sample to 32.6 at.% following the 63-h exposure, and the silicon concentration increases from 8.1 to 11.1 at.% after 63 h. The data reveal the formation of a silica layer on the surface, which serves as a protective barrier preventing further degradation of the polymer underneath with increased exposure to the O-atom flux.

Keywords: Atomic oxygen; POSS; silsesquioxane; polymer; space; space materials.

1. INTRODUCTION

Polymeric materials offer many advantages for low earth orbit (LEO) applications including ease of processing and reduced payload-to-orbit costs from the reduction in weight. However, over the last two decades it has been well established that poly- mers used in the construction of space vehicles undergo severe degradation resulting

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in reduced spacecraft lifetimes. These materials degrade because spacecraft surfaces must endure high fluxes of hyperthermal atomic oxygen (AO), bombardment by low and high-energy charged particles, thermal cycling, and the full spectrum of solar radiation. AO is formed by the dissociation of molecular oxygen by ultraviolet radiation from the sun, resulting in an AO concentration of approximately 10^8 atom/cm^3. The reverse reaction in which an oxygen molecule forms from AO does not have a high reaction rate because it requires a teratomic collision. The third atom is required to carry away the energy released by formation of O_2. For this reason the predominant species in LEO is AO. The actual flux of $\sim 10^{15}$ atom/cm^2-s impinging on a spacecraft is high due to orbiting speeds of approximately 8 km/s. At these relative speeds AO particles collide with a kinetic energy of ~ 5 eV. These energetic collisions not only result in surface chemical reactions, but can also lead to a physical sputtering of the surface species. Many studies have been conducted in an effort to determine the mechanism of this degradation primarily caused by surface reactions with AO [1–9]. However, these studies have all been carried out after exposing these highly reactive surfaces to air prior to analysis, thus introducing artifacts that do not represent the true nature of space. Recent studies have shown that exposure to air chemically alters the reactive surfaces formed during AO exposure [10, 11]. It is, therefore, essential that analysis of polymers exposed to AO be carried out *in situ* to avoid artifacts induced by air exposure.

In this study a solvent-cast film of polyhedral oligomeric silsesquioxane (POSS)–polyurethane (PU) copolymer has been characterized *in situ* using X-ray photoelectron spectroscopy (XPS) before and after incremental exposures to the flux produced by an electron stimulated desorption (ESD) AO source [12]. POSS molecules are hybrid inorganic/organic structures synthesized from the self-condensation reactions of alkyl trichlorosilanes. Over the last 7 years, Lichtenhan and coworkers have focused on incorporating POSS frameworks into traditional polymer systems via copolymerization, grafting, and blending processes [13–19]. Three primary POSS-polymer architectures (bead, pendant, or cross-linked) are available for use in thermoset systems or in copolymerizations as shown in Fig. 1. Significant property enhancements have been reported for these hybrid polymers including increased use temperature, increased toughness, decreased flammability, and increased oxidation resistance. These property enhancements are attributed to the nano-level interaction of the POSS framework with the polymer matrix. Traditionally, silica fillers have been used in polymer applications requiring alterations in physical and mechanical properties such as tensile strength, abrasion, and fatigue resistance. In addition to numerous property enhancements, POSS polymers have lower densities (1.2–1.5 g/cm^3) than silica fillers (2.4–2.6 g/cm^3) [20, 21]. Unlike silica fillers, POSS frameworks can be easily functionalized for polymer compatibility without significantly affecting processing conditions. Compared to silica fillers, POSS hybrid polymers are able to impart similar property enhancements, including many not possible utilizing filler technology. Previous studies have also shown that Si-O systems exhibit a superior resistance to AO degradation due, in part, to their ox-
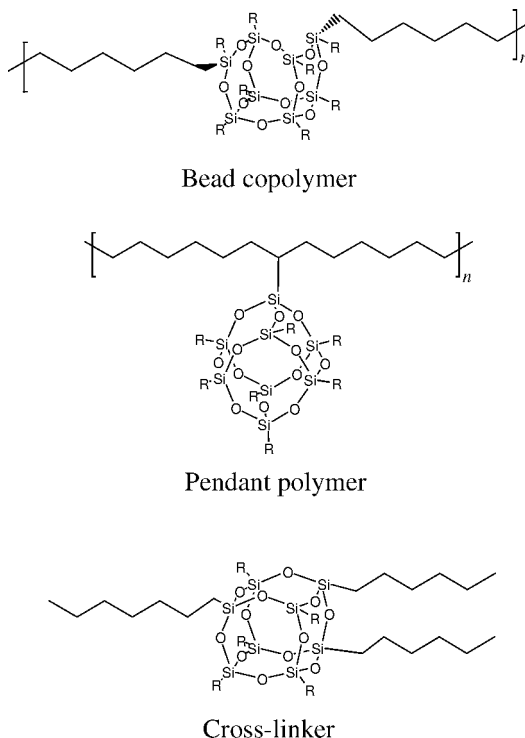
Bead copolymer

Pendant polymer

Cross-linker

Figure 1. POSS-polymer structures. POSS in cross-linking configuration (bottom), in a pendant configuration (middle), and in a bead configuration (top).

ophilicity and high bond strength (~8 eV) [22, 23]. However, pure siloxane systems have displayed many disadvantages for space applications including the generation of volatile cyclic species when exposed to AO that can recondense on optical surfaces [24]. Recent testing of POSS-containing polymers has shown promising AO resistant properties. *In situ* XPS analysis has revealed that upon exposure to AO these hybrid organic/inorganic polymers rapidly form a ceramic-like, passivating SiO_2 layer that prevents further degradation of the underlying polymer [25, 26]. Similar observations are reported for the POSS–PU sample examined in this study.

2. EXPERIMENTAL

2.1. O-atom source characteristics

The ESD source used in this study was developed by Hoflund and Weaver [12]. It is ultrahigh vacuum (UHV) compatible, operates with the sample at room temperature and produces a high-purity, hyperthermal, AO flux with an AO: O^+ ratio of ~10^8. These sources are superior to plasma sources in that they produce hyperthermal, ground-state O atoms and operate at UHV pressures (~1.33×10^{-7} Pa) with negligible amounts of other species, including ions, contaminants,
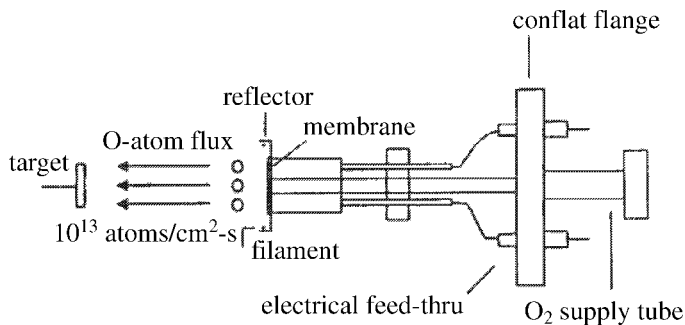
Figure 2. Schematic diagram of the hyperthermal atomic oxygen source.

and UV radiation. The operational concept of the hyperthermal AO generator is shown in Fig. 2. Ultrahigh purity molecular oxygen dissociatively adsorbs on a metallic Ag alloy membrane at the high-pressure side and permeates at elevated temperature ($\sim$400°C) to the UHV side. There the adsorbed atoms are struck by a directed flux of primary electrons, which results in ESD of AO forming a continuous flux. Many processes have to function in series at sufficiently high rates for the system to work, including dissociative adsorption of the molecular gas on the metal surface, permeation of atoms through the membrane, and formation of the neutral flux by ESD. Some bremsstrahlung radiation is produced by the electrons striking the Ag membrane. Because the UV component is small, this radiation has only a small effect on the chemical processes occurring at the sample surface. Another potential problem is the sublimation of Ag from the membrane surface which could accumulate on the sample surface. Studies have been performed to optimize the power input to the membrane surface so that the AO flux is maximized while the Ag sublimation rate is negligible. This is possible because the Ag sublimation rate decreases exponentially with temperature.

The O atoms produced by this source have been shown to be hyperthermal, but their energy distribution has not been measured. Corallo *et al.* [27] have measured the energy distribution of O ions emitted by ESD from a Ag(110) surface and found that this distribution has a maximum of $\sim$5 eV and a full-width at half maximum of 3.6 eV. This ion energy distribution would set an upper bound for the neutral energy distribution because ESD neutrals are generally believed to be less energetic than ESD ions. This point has been discussed often in the ESD literature but not actually demonstrated. A mass spectrometer has been used to characterize the flux produced by this ESD source. The ion acceleration potential was set at 0.0 V in these studies. Since calibration studies demonstrated that the ions entering the quadrupole section had to have a minimum kinetic energy of 2.0 eV to reach the detector, the ESD neutrals have a minimum energy of 2 eV. Therefore, the hyperthermal AO produced by this ESD source have energies greater than 2 eV but possibly less than the ion energy distribution.

2.2. Preparation of the 20-wt% POSS–PU copolymer

PU samples were synthesized by a two-step solution reaction (Fig. 3) described by Hsiao *et al.* [28]. Diphenylmethane-4,4′-diisocyanate (MDI) and polytetramethylene glycol (PTMG) ($M_w = 2000$) were mixed in a molar ratio of 2 : 1 and prepolymerized at 80°C for 2 h. The prepolymer was dissolved in anhydrous polytetrahydrofuran (PTHF). The prepolymer was then chain extended by addition of POSS-TMP diol at room temperature over 6 h. The mixture was cooled to 5°C and 1,4-butanediol (BDO) added drop-wise. The system was warmed to room temperature and after 1 h the products were precipitated in a 1 : 1 methanol–water solution, separated by filtration and dried in vacuo. All the reactions were carried out under nitrogen.

2.3. Preparation of thin films by solvent casting

Thin films of the 20-wt% POSS–PU were made by solvent casting THF solutions of 5 mg/ml concentration of each polymer onto 1 cm × 1 cm aluminum substrates. The films were dried at room temperature for 24 h. The aluminum substrates were cleaned with Boraxo™ soap and water, rinsed with deionized water, followed by ultrasonic cleaning in toluene, acetone, trichloroethylene, acetone, and ethanol successively.

2.4. Surface characterization

A solvent-cast 20-wt% POSS–PU film was wiped with isopropanol and inserted into the UHV chamber (base pressure $< 1.33 \times 10^{-7}$ Pa). XPS measurements were performed using a double-pass cylindrical mirror analyzer (DPCMA) (PHI Model 25-270AR). XPS survey spectra were taken in the retarding mode with a pass
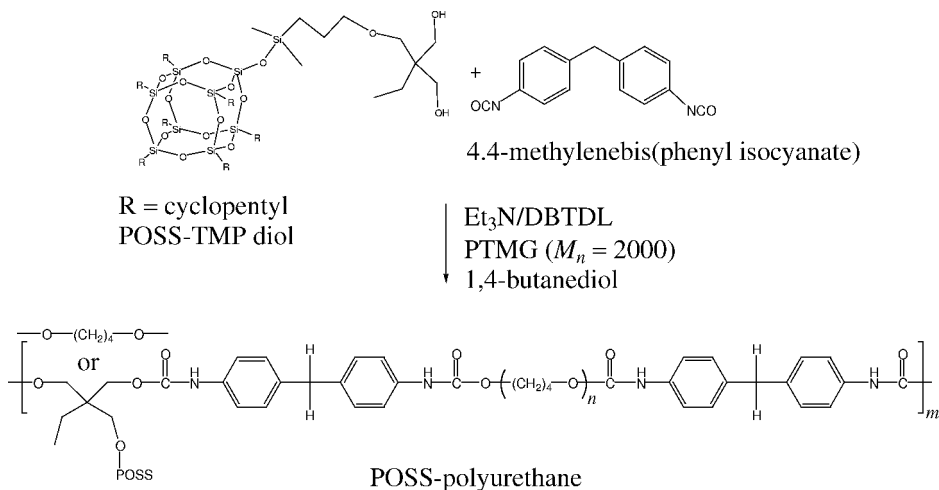

Figure 3. Scheme for synthesis of POSS–PU.

energy of 50 eV, and high-resolution XPS spectra were taken with a pass energy of 25 eV using Mg K_α X-rays (PHI Model 04-151 X-ray source). Data collection was accomplished using a computer interfaced, digital pulse-counting circuit [29] followed by smoothing with digital-filtering techniques [30]. The sample was tilted 30° off the axis of the DPCMA, and the DPCMA accepted electrons emitted into a cone $42.6 \pm 6°$ off the DPCMA axis.

XPS spectra were first obtained from the as-entered, solvent-cleaned sample. The sample was then transferred into an adjoining UHV chamber that houses the ESD AO source via a magnetically coupled rotary/linear manipulator. There the surface was exposed to a hyperthermal AO flux and re-examined without air exposure after total exposure times of 2, 24, and 63 h. The approximate normal distance between the sample face and source in this study was 15 cm, at which distance the flux was about 2.0×10^{13} atom/cm^2-s for the instrument settings used. The flux was determined based on the growth rate of metal oxide films in which the metal deposition rate was known and stoichiometric oxides were formed [31, 32]. The sample was maintained at room temperature during the AO exposures with a slight temperature increase to 50°C due to exposure to the X-ray source during XPS data collection. The substrate temperature was determined using a chromel-alumel thermocouple. After the 63-h AO exposure, the sample was exposed to air (room temperature, ~22°C, relative humidity ~60%) for 4 h and again examined using XPS.

3. RESULTS AND DISCUSSION

XPS survey spectra obtained from an as-received, solvent-wiped 20-wt% POSS–PU surface before and after the 2, 24, and 63 h O-atom exposure are shown in Fig. 4a–d, respectively. The spectrum Fig. 4e was taken after the 4-h air exposure following the 63-h AO treatment. The peak assignments shown in Fig. 4 pertain to all five spectra. The predominant peaks apparent in these spectra include the C 1*s*, O 1*s*, Si 2*p*, Si 2*s*, O 2*s*, N 1*s*, Sn 3*d*, and the Na and O Auger peaks. The presence of Sn is due to the catalyst system (dibutyltindilaurate) used during polymer synthesis. Na is present in parts per million levels in the reactants used to make the catalyst system and migrates to the surface as a result of AO exposure and affinity for silica. Significant changes in relative peak heights are observed for the C, O, and Si features following the AO exposures. Estimates of the near-surface compositions have been made from the peak areas in the high-resolution spectra using published atomic sensitivity factors [33] with the assumption of a homogeneous surface region. The compositions determined in this manner are presented in Table 1 for the as-entered, AO-exposed and air-exposed surfaces.

XPS probes the near-surface region of the sample and yields a weighted average composition, with the atomic layers near the surface being weighted more heavily since the photoemitted electrons from these layers have a lower probability of scattering inelastically. The sampling depth is ~4–6 nm, and ~10% of the
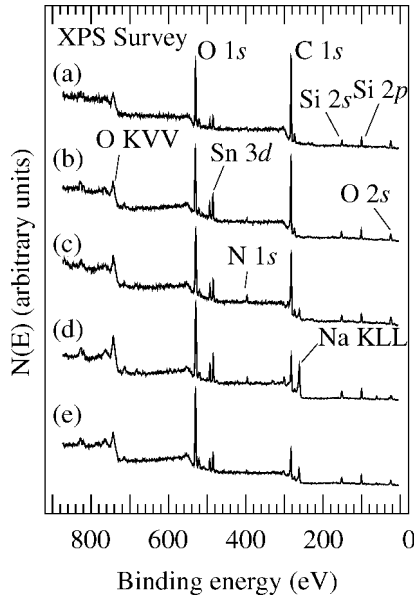
Figure 4. XPS survey spectra obtained from a solvent-cleaned, 20-wt% POSS–PU film after insertion into the vacuum system (a), after 2 h (b), 24 h (c), and 63 h exposure to the hyperthermal AO flux (d), and 4-h air exposure following the 63-h AO exposure (e).

Table 1.
Near-surface composition determined from XPS data obtained from the as-entered, solvent cleaned, AO, and air-exposed 20-wt% POSS–PU sample

Surface sample treatment	AO fluence, O/cm^2	Composition (at.%)						Atom ratio
		O	Si	C	Sn	Na	N	O/Si
As-entered, solvent cleaned	—	18.5	8.1	72.5	0.9	—	—	2.28
2-h AO exposure	1.44×10^{17}	20.4	7.9	70.7	1.0	—	—	2.58
24-h AO exposure	1.77×10^{18}	21.8	9.5	61.7	1.0	3.0	3.0	2.29
63-h AO exposure	4.53×10^{18}	32.6	11.1	37.8	1.8	13.6	3.1	2.93
4-h air exposure following 63-h AO exposure	4.53×10^{18}	38.9	13.7	43.4	2.0	2.0	—	2.83

signal originates from the outermost atomic layer [34]. This near-surface region is nonhomogeneous because the AO reacts with the outermost few atomic layers. Therefore, the region that is affected to the greatest extent as a result of the reaction with AO also makes the largest contribution to the XPS signal. This fact implies that XPS is an excellent technique for studying AO erosion of spacecraft materials. Even though the distribution functions involving the depth of chemical reactions in the near-surface region and the XPS determination of the weighted average composition of the near-surface region are complex, the compositional values provide a trend which is indicative of the chemical alterations occurring during AO exposure. The

compositions determined using the homogeneous assumption are shown in Table 1 as a function of AO fluence.

The O/Si atomic ratio is 2.28 for the as-entered sample; increases to 2.58, decreases to 2.29 and again increases to 2.93 after the 2, 24, and 63 h AO exposures respectively. After the 4-h air exposure, the O/Si atomic ratio is 2.83, but C also accumulates on the surface during the air exposure. The decrease in the O/Si ratio to 2.29 after 24 h of exposure could be attributed to the relative increase of Na and Sn on the surface. However, the overall increase in the O/Si atomic ratio resulting from exposure to the AO flux is a trend that has previously been observed in two other similar studies of a POSS–PDMS (polydimethylsiloxane) and 60-wt% POSS–PU copolymer [25, 26]. It is attributed to the formation of SiO_2 and is consistent with the high-resolution spectra that follow. A significant reduction in the C 1s peak is observed as a result of the incremental exposures to the O-atom flux. The near-surface C concentration decreases from 72.5 at.% for the as-entered sample to 37.8 at.% after the 63-h exposure. This decrease in C is most likely due to the reaction of C in the near-surface region with O to form CO and/or CO_2 which desorb. The increase in the C concentration to 43.4 at.% observed after the air exposure is most likely due to the adsorption of C-containing molecules from the air. Hydrogen in the POSS would also react with the AO to form water which would desorb.

High-resolution XPS C 1s, O 1s and Si 2p spectra obtained from the as-received, solvent-wiped surface before and after the 2, 24, and 63 h AO exposures are shown in (a)–(d) of Figs 5, 6, and 7, respectively. Spectrum (e) was obtained after the 4-h air exposure following the 63-h AO exposure. Variations in peak shapes and positions are observed between the nonexposed, AO-exposed, and air-exposed surfaces, indicating that the chemical species distribution is altered by exposure to the AO flux and then to air. No surface charging of the sample was evident during the experiment as this would have resulted in a significant binding energy (BE) shift. Differential charging also results in peak broadening or even peak multiplicity. This was not observed in this study.

The C 1s peak, shown in Fig. 5a, is broad and centered at 285 eV, indicating that the predominant form of carbon present for the as-entered sample is aliphatic, located on the hard and soft segments of the polymer chain and the cyclopentyl groups on the POSS cages [35]. In spectra (b)–(d), the C 1s peak becomes broader, displaying visible shoulders with increasing exposure to the AO flux. A shoulder due to aromatic carbon is present in these spectra at 284.7 eV. Shoulders are also visible on the high BE side of the C 1s peak in spectra (b)–(d). These probably are due to species such as alcohols, formaldehydes (BE $\sim$286.0–287.7 eV), and organic acids (BE $\sim$287.5) which form by reaction with the AO flux. These changes coincide with a decrease in the total carbon concentration in the near-surface region from 72.5 to 37.8 at.%. Large reductions in the carbon concentrations after AO exposure were also observed in the POSS–PDMS and 60-wt% POSS–PU samples studied previously [25, 26]. The data indicate the selective removal of
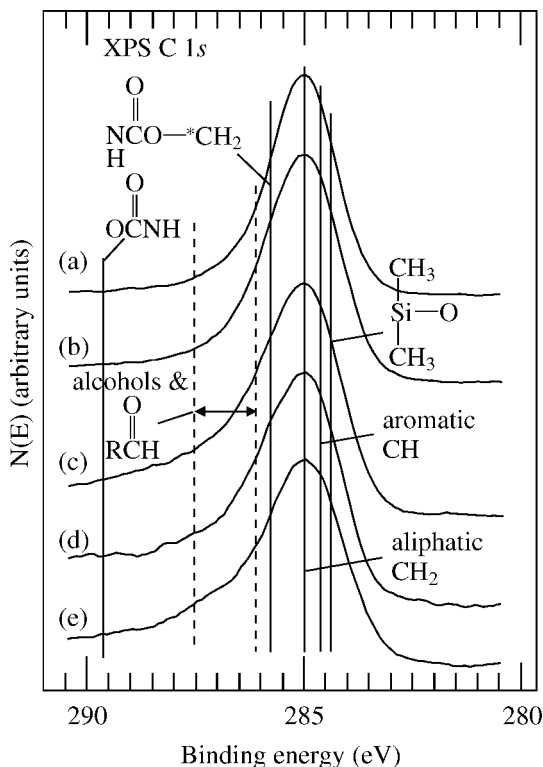
Figure 5. XPS C 1*s* spectra obtained from a solvent-cleaned, 20-wt% POSS–PU film after insertion into the vacuum system (a), after 2 h (b), 24 h (c), and 63 h exposure to the hyperthermal AO flux (d), and 4-h air exposure following the 63-h AO exposure (e).

the cyclohexyl or cyclopentyl groups surrounding the POSS cages. Exposure to air (spectrum (e)) results in a 5.6 at.% increase in C. The AO exposure generates reactive surface sites which apparently adsorb hydrocarbons from the air.

The O 1*s* spectra obtained from the as-entered sample is shown in Fig. 6a. This peak is broad and centered at 532.1 eV. The predominant form of oxygen present for the as-entered sample corresponds to the carbonyl in the urethane segment (531.9 eV) of the polymer and the oxygen present in the POSS cages (532.0 eV). The oxygen content on the surface gradually increases with increasing exposures to the AO flux. After 63 h total exposure the oxygen content increases from an initial 18.5 to 32.6 at.%. This increase coincides with the O 1*s* spectra in (b)–(d) shifting to a higher BE corresponding to the formation of silica on the surface. This trend was observed and reported in the two previous [25, 26] studies on the POSS–PDMS and 60-wt% POSS–PU copolymers. Na also migrates to the surface from the bulk of the polymer as the silica layer is being formed. After 63 h the Na concentration is 13.6 at.%. Exposure to air results in a 6.3-at.% increase in the surface O content as the reactive surface adsorbs hydrocarbons from the air, changing the relative composition on the surface of the polymer. However, the peak remains centered
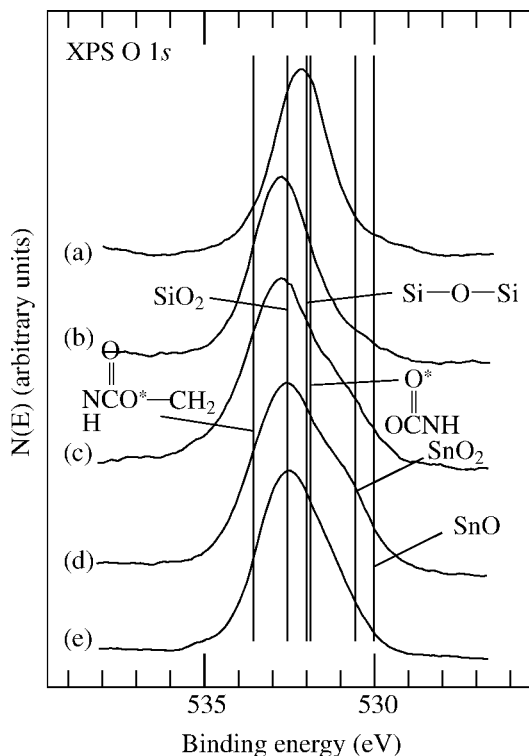
Figure 6. XPS O 1*s* spectra obtained from a solvent-cleaned, 20-wt% POSS−PU film after insertion into the vacuum system (a), after 2 h (b), 24 h (c), and 63 h exposure to the hyperthermal AO flux (d), and 4-h air exposure following the 63-h AO exposure (e).

at the binding energy corresponding to SiO_2, thus indicating that the silica layer formed is chemically stable. This conclusion is corroborated by the Si 2*p* spectra discussed next.

The Si 2*p* peaks obtained from the sample after the various treatments are shown in Fig. 7. The Si 2*p* peak for the as-entered sample (spectrum (a)) is broad, indicating the presence of several chemical states of silicon. This peak is centered at a BE of 102.7 eV, which corresponds to $RSiO_{1.5}$ in the POSS cage. However, spectra (b)−(d) reveal the formation of a SiO_2 layer with incremental exposures to the AO flux. The fact that little difference is observed in the spectra obtained after the 24- and 63-h exposures indicates that this silica layer forms a protective barrier on the surface which prevents further degradation of the polymer with longer exposure to the AO flux. The 5-eV AO is not energetic enough to penetrate more than one or two atomic layers into the polymer, while XPS probes as deeply as 4−6 nm beneath the surface. The significant compositional changes observed indicate that most of the near-surface region examined by XPS is altered by the AO exposure. The chemical reactions, which form CO and/or CO_2 and H_2O are exothermic, so the local surface temperature may be relatively high. This and the fact that the AO
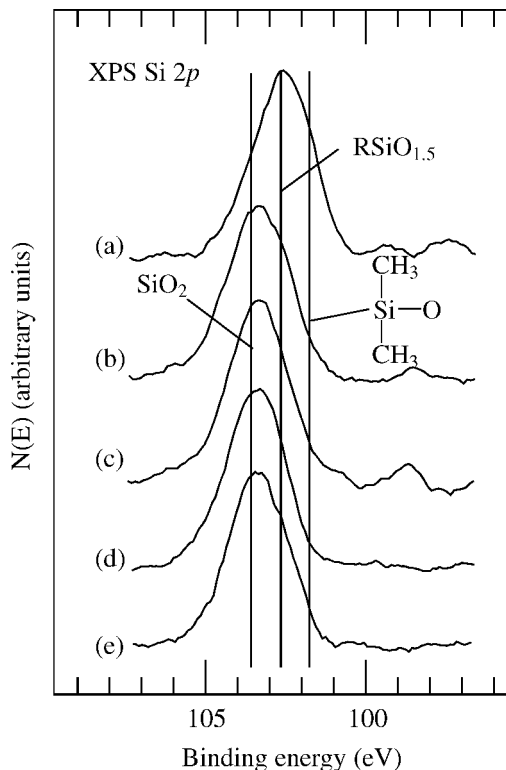
Figure 7. XPS Si 2*p* spectra obtained from a solvent-cleaned, 20-wt% POSS–PU film after insertion into the vacuum system (a), after 2 h (b), 24 h (c), and 63 h exposure to the hyperthermal AO flux (d), and 4-h air exposure following the 63-h AO exposure (e).

causes a chemically-induced driving force result in diffusion of subsurface C and H to the surface where they react with the AO. This mechanism is responsible for the subsurface compositional alterations observed using XPS.

4. SUMMARY

The surface of a film of a POSS–PU copolymer has been characterized *in situ* using XPS before and after exposure to different fluences of AO produced by an ESD hyperthermal oxygen atom source. The XPS data indicate that exposure to AO reduces the carbon content on the surface from 72.5 to 37.8 at.% after 63 h exposure to an AO flux of 2.0×10^{13} atom/cm^2-s. The oxygen and silicon concentrations in the near-surface region determined using XPS increase with increasing exposure to the AO flux. The oxygen-to-silicon ratio increases from 2.28 for the as-entered sample to 2.93. High-resolution XPS data suggest that the AO initially attacks the cyclopentyl groups on the POSS cage most likely forming CO and/or CO_2 and water which desorb. Increased exposure to the AO flux results in the formation of a silica layer on the surface which acts as a protective barrier preventing further

degradation of the underlying polymer. Exposure to air also results in the adsorption of hydrocarbon species on the reactive surface formed by exposure to AO.

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